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Catalytic activity and chemical structure of Nano MoS₂ synthesized in a controlled environment

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A novel hydrothermal method for preparation of nano MoS₂ for hydrodesulfurization (HDS) with MoO₃ as precursors is presented. The redox reaction mechanism is, for the first time, revealed. It is shown to involve the oxidation of S²⁻ to SO₄²⁻ while hexavalent Mo is reduced to quadrivalent Mo to form MoS₂. HS⁻ group is identified to play a key role in reduction of MoO₃. The acid-base behaviour of Na₂S to HS⁻ group and the yield of the resulting MoS₂ are controlled via the pH of the synthesis solution. Various characterization methods, e.g. XRD, TEM, SEM, BET, TPR, XPS, XANES, EXAFS, etc. are employed for the characterization of the synthesized MoS₂. The results show that high purity MoS₂ is obtained. The ratio of precursors, MoO₃ and Na₂S, influences the crystal structure and catalytic activity. Slight less sulfur than stoichiometric ratio of S/Mo produces defect sites, which promotes catalyst activities in the hydrodesulfurization of real light cycle oil (LCO).

Introduction

Nano-scaled molybdenum disulfide (MoS₂) has a layered structure with individual sheets strongly covalently bonded within but held together through weak van der Waals interactions. This results in two distinct surfaces of MoS₂: basal and edge planes. Within a layer, each Mo (IV) center is bonded to six sulfurs forming a trigon prismatic coordination while every sulfur atom is connected with three Mo forming pyramidal interstices^{1,2}. The unique structure and chemistry properties make MoS₂ widely applied as a functional material in diverse fields of lubrication, electronic transistors, batteries, photovoltaics, catalysis, and sensing³. MoS₂ also shows high activity in hydrodesulfurization reaction⁴.

There are different methods for synthesis of nano MoS₂ including solid-gas sulfidation, thermal decomposition, and solution reactions⁵. Hydrothermal method is an alternative route to preparing nano MoS₂ with MoO₃ as precursor⁶. Compared to thiomolybdate, MoO₃ is an attractive precursor as it is cost-effective. MoO₃ has been used as precursor to synthesize nano MoS₂ of different morphologies, e.g. nano-sheet⁴, nanowires⁷, nanotubes and nanorods⁸. Our previous study discussed the effect of temperature on the nucleation and growth process⁶. A relationship has been established between the crystallization process and MoS₂ structure. Successful production of nano MoS₂ through hydrothermal route is associated with a number of synthesis parameters such as pH of solvent, precursor

concentration, and temperature. However the reaction mechanisms for formation of MoS₂ are poorly understood.

This work tends to address this deficiency. In particular, the role of reducing agent in transformation of hexavalent Mo to quadrivalent Mo to form MoS₂ will be studied. The reaction mechanism of the nano MoS₂ formation is discussed. Appropriate synthesis condition results in high yield of highly dispersed nano MoS₂ crystalline that has high hydrodesulfurization activity. The textural and chemical structure of synthesized catalysts were extensively characterized by various techniques, e.g. TEM, BET, XRD, XPS, TPR and XAFS, etc. The hydrodesulfurization (HDS), hydrodenitrogenation (HDN) activities were evaluated using a real diesel fraction - light cycle oil (LCO).

Experimental Section

Preparation of MoS₂ catalysts. A series of molybdenum sulfide catalysts were synthesized using MoO₃ (STEM Scientific) and Na₂S·9H₂O (Fisher Scientific) as precursors⁶. 14.4 grams of MoO₃ was used in the synthesis. Different molar ratios of Na₂S to MoO₃ were employed and listed in Table 1. Na₂S·9H₂O and MoO₃ were gradually dissolved in deionized water and 4M HCl was added dropwisely to adjust the pH of the solution. The mixture was then transferred into autoclave and reacted for 2 h at 320 °C at 500 rpm in nitrogen or hydrogen atmospheres. The resultant black solid was filtered, washed using deionized water and ethanol, and then dried under nitrogen protection at 150 °C for 4 h. The catalyst recovery rate was calculated based on theoretical MoS₂ yield (Equation 1). The prepared MoS₂ catalysts at various Na₂S to MoO₃ molar ratios were denoted as CAT-x (where x stands for the molar ratio of Na₂S to MoO₃). pH values of the initial synthesis solution and the final filtrate were determined using a pH meter (AB 15, Fisher Scientific). The concentrations of sulfur anions S₂O₃²⁻ and SO₄²⁻ in the filtrate

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were determined by an ion chromatography (DIONEX, DX-120). The reference MoS₂ was purchased from SPI supplies.

$$\text{Recovery} = \frac{\text{Actual } W_{\text{MoS}_2}}{\text{Theoretical } W_{\text{MoS}_2}} \times 100\% \quad \text{Equation 1}$$

Catalyst characterization. The transmission electron microscopic (TEM) images were recorded on a JEOL 2011 STEM (JEOL Ltd., Tokyo, Japan) operated under high-resolution mode and 200 keV electronical energy. The average length and thickness of MoS₂ crystals calculated using Equations 2 and 3 were expected values. At least 200 images of different MoS₂ particles (particle' refers to one MoS₂ crystalline) were used. The morphology of catalysts was also observed by Scanning electron microscopy (JEOL JSM6400 SEM).

$$\text{Average thickness } \bar{T} = \frac{\sum_{i=1,2,\dots} N_i T_i}{\sum_{i=1,2,\dots} N_i} = \frac{\sum_{i=1,2,\dots} N_i T_i}{N} \quad \text{Equation 2}$$

$$\text{Average length } \bar{L} = \frac{\sum_{i=1,2,\dots} N_i L_i}{\sum_{i=1,2,\dots} N_i} = \frac{\sum_{i=1,2,\dots} N_i L_i}{N} \quad \text{Equation 3}$$

where T , L , and i stand for thickness, length, and number of layers, respectively. \bar{T} is the expected value of particle thickness and \bar{L} is the expected value of particle length. It is assumed that all i -th layered particles have the same thickness (T_i). The length of i -th layered particles, L_i , is an average length of the particles that have the same numbers of layers (i). N_i denotes the number of i -th layered particles and N represents the total number of particles.

The measurement of nitrogen adsorption-desorption isotherm was conducted on Autosorb-1 (Quantachrome Instruments). The specific surface area of catalyst was determined using the Brunauer-Emmett-Teller (BET) method. The total pore volume was calculated from the volume of nitrogen adsorbed at the relative pressure p/p_0 0.995. Pore size distribution was analyzed from the isotherms by the Barrett-Joyner-Halenda (BJH) method.

The synthesized products were identified by the X-ray diffraction (XRD) pattern, which were recorded on a diffractometer (Bruker AXS D8 XRD) using CuK α radiation with the 2θ range of 5–85° and the scan speed of 1°/min.

The elemental analysis for molybdenum and sulfur was conducted on a JEOL-733 Superprobe, operating at 15 keV and 100 nA.

Temperature programmed reduction (TPR) was conducted on Autosorb-1 (Quantachrome Instruments). 100 mg catalyst was added in a quartz tube and heated to 700°C at a rate of 10°C/min, under a 50 ml/min flow of 2% H₂ in Ar. The consumption of H₂ and production of H₂S was monitored by a mass spectrometer (RGA 200 Stanford Research Systems, Inc.).

The XPS measurements were performed on an AXIS 165 spectrometer (Kratos Analytical, University of Alberta). The base pressure in the analytical chamber was lower than 3×10^{-8} Pa. Monochromatic Al K α source ($h\nu = 1486.6$ eV) was used at a power of 210 W. The analysis spot was 400 \times 700 μm . The resolution of the

instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks. The survey scans were collected for binding energy extending from 1100 eV to 0 with pass energy of 160 eV and a step of 0.4 eV. 20 eV with a step of 0.1 eV was used for the pass-energy for high-resolution spectra. The number of scans varied from 3 to 30 to ensure a good signal to noise ratio.

The X-ray absorption near edge structure (XANES) spectra were obtained at a Soft X-ray Microanalysis Beamline (SXRMB) of the Canadian Light Source (CLS; Saskatoon, SK, Canada) equipped with a Si (1 1 1) double crystal monochromator. CLS, a 2.9 GeV, third generation storage ring, presently operates with an injection current of 250 mA. Samples were sulfided at 280°C in H₂ with dimethyl disulfide (DMDS) for 2h prior to measurement. Catalyst powders were uniformly dispersed on double-sided conducting carbon tapes under a dry nitrogen atmosphere. The measurements of S K-edge and Mo L₃-edge were made in total electron yield by recording the sample drain current. Data analysis of the XANES spectra was performed using Athena software. Mo K-edge EXAFS spectra were recorded in the transmission mode at room temperature. Fourier transformation of the k/f (k) weighted EXAFS data for $\Delta k = 14 \text{ \AA}^{-1}$ ($3 < k < 17$) was performed to obtain the radial distribution function around Mo. Detailed procedure was described elsewhere⁸.

Hydrodesulfurization evaluation. A batch reactor (Parker Autoclave Engineers) was employed in this experiment. A light cycle oil (LCO) with 1.46% S and 156 ppm N provided by a local refinery was used as feedstock. When the reactor was heated to 375 °C, LCO was introduced into the reactor. The weight ratio of catalyst to oil is 1:200. The hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) took place at 375 °C under H₂ gas pressure of 1400–1500 psi and 1000 rpm.

The total sulfur and nitrogen concentrations of the feedstock and the hydrotreated products were measured by a Sulfur/Nitrogen analyzer (9000 series, Antek Instruments Inc). The sulfur species were analyzed by a gas chromatography (GC) equipped with a non-polar VF-1ms capillary column (15 m \times 0.25 mm \times 0.25 μm , max temperature: 325°C) and a PFPD detector (Varian 450). The following temperature profile was used: 2 min at 120°C, followed by a linear increase at 6°C /min to 170°C and a further increase at 20°C /min to 290°C, kept for 2 min. Density of the liquid oil was measured by a portable density meter (DMA 35N, Anton Paar GmbH, Graz, Austria) following ASTM 4052. The HDS/HDN conversion was calculated by subtracting the sulfur/nitrogen in the feed from product and divided by the sulfur/nitrogen in the feed. The calculation of rate constant k was based on pseudo-first order reaction.

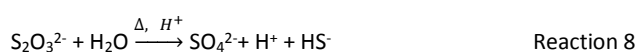
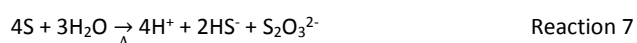
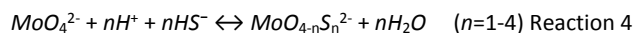
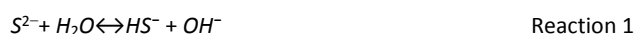
Results and discussion

Synthesis of MoS₂ in controlled medium. A series of MoS₂ were synthesized in a medium of controlled pH values. The experimental parameters are shown in Table 1. MoO₃ and Na₂S serve as molybdenum and sulfur sources, respectively. Without addition of HCl, precursor Na₂S is first mixed in deionized water. Then MoO₃ powders were slowly stirred in and completely dissolved in the

basic solution. A clear yellow liquid with pH=12.59 was resulted, which liquid was then transferred to an autoclave for 2 hour hydrothermal reaction at 320°C. No solid catalyst was produced (entry 1). HCl was used to adjust the pH of resulted liquid mixture for all other entries. The clear yellow liquid turns to be dark red or brown once HCl was dropped in. Slightly reducing initial pH of the Na₂S-MoO₃ solution from 12.59 to 10.61, a small amount of dark solid product was detected after the 2-hour synthesis (entry 2). The single 002 diffraction peak shown in the XRD pattern (Figure 1) confirmed that the solid product was amorphous MoS_x. Continuous adjustment of the Na₂S-MoO₃ solution to pH=5.70 (entry 3) leads to a satisfactory result. The yield of MoS₂ reached as high as 96% of its theoretical value. The obtained MoS₂ also shows satisfactory crystallinity as indicated by the XRD pattern (Figure 1). Further acidification of the Na₂S-MoO₃ solution to pH=0.95 lead to an unsuccessful synthesis (entry 4) with significant amount of MoO₂ identified. This finding suggests that the initial pH of synthesis solution plays a key role in formation of nano crystalline MoS₂.

Gaseous environment is also a factor that influences the conversion from MoO₃ to MoS₂. With inert gas (nitrogen) filled in the reaction chamber, Na₂S (S²⁻) acted as reduction agent and crystallized MoS₂ was successfully synthesized (entry 3, 5 and 6). However, reductive gas, e.g. hydrogen gas, can replace Na₂S, function as a reduction agent during the synthesis, reducing MoO₃ to MoO₂ instead of formation of MoS₂ (Figure 1). Compared to entries 5 & 6, entry 7 has a very high pH of filtrate suggests little consumption of Na₂S during the synthesis (Table 1). Reductive gas atmosphere has negative impact on the formation of crystallized MoS₂.

Synthesis reactions: identification of the key role of H⁺ and HS⁻. In the hydrothermal synthesis, crystalline MoS₂ is formed from the redox reaction of MoO₃ and Na₂S, where Mo is reduced from Mo⁶⁺ to Mo⁴⁺. Sodium sulfide is hydrolyzed in water to give strong alkaline solutions, as shown in Reaction 1 and Reaction 2. Due to acid nature, MoO₃ is easily dissolved in the basic solution to give MoO₄²⁻ (Reaction 3), forming a clear yellow solution, as seen in entry 1 of Table 1. Unfortunately, MoO₄²⁻ group is not directly responsible for the precipitation of solid MoS₂.



Addition of a few drops of HCl darkens the solution. Continuous titration of acids leads to precipitation of solids (entry 2), which is confirmed to be molybdenum sulfides (amorphous). H⁺ appears to be a likely mechanistic requirement for the solid precipitation. It is known that MoO₄²⁻ could react with H⁺ and HS⁻ to form tetrahedral sulfido-molybdenum complexes such as MoOS₃²⁻, MoO₂S₂²⁻, MoO₃S²⁻ and MoS₄²⁻¹⁰. This is a [H⁺]-dependent process and high [H⁺] is beneficial to O removal. The HS⁻ was confirmed to be an effective incoming nucleophile to interact with O²⁻ on Mo (VI)¹⁰. Sufficient [H⁺] and [HS⁻] is then led to initial precipitation of MoS_x at room temperature⁵, which is the seed for production of crystal MoS₂⁷. Reaction 4 and Reaction 5 are proposed to describe the process.

HS⁻ group plays a key role in the redox reaction. The hydrolysis of sulfide ion gives three species: S²⁻, HS⁻ and H₂S. Given the ΔH and ΔG¹⁶, rate constants can be calculated and then the molar concentrations of the three species at different pH can be determined. The theoretical acid-base behaviour of the S²⁻, HS⁻ and H₂S as a function of pH are shown in Figure 2. In strong alkaline solutions, sulfide ion presents in the deprotonated form as the sulfide dianion, S²⁻ while in strong acid environment, it exists in the form of H₂S. HS⁻ becomes inadequate in both strong acid and strong alkaline synthesis solution. Without sufficient HS⁻ Reaction 4 most likely stops and thus formation of intermediate complexes MoO_{4-n}S_n²⁻ becomes limited. The presence of S²⁻ in strong alkaline solution cannot facilitate Reaction 4 to proceed (entry 2). This suggests that S²⁻ plays no role in formation of MoS₂. With strong acid solution, large amount of H₂S produced and remains in gaseous phase due to its poor solubility in acidic solution. A certain amount of MoO₂ is formed (entry 4). On the other hand, HS⁻ is produced in mild acid solution (entry 3, 5 and 6) and good yields of MoS₂ are obtained. Therefore, the formation and the production yield of crystalline MoS₂ is highly associated with [H⁺] and [HS⁻]. Both insufficient [H⁺] and overdose [H⁺] generate inappropriate pH of the synthesis solution, which results in unsatisfactory concentration of HS⁻ and then little MoS₂ can be produced. Species HS⁻ presents in neutral and basic solutions at room temperature. The pH for HS⁻ group shifts to lower values at the hydrothermal synthesis temperature, 320°C, with an optimal range falling between 6 and 8. It is fair to comment that formation of MoS₂ is a [H⁺] and [HS⁻] dependent process. Up to this point, it seems that both weak acid and basic initial solutions are suitable for MoS₂ synthesis. A further discussion presents below to interpret whether mild acid or mild basic solution is optimal for the production of MoS₂.

At synthesis temperature, 320°C, the precipitated solid MoS₃ from Reaction 5 is reduced to MoS₂ accompanying by production of sulfur element in Reaction 6 (Sulfur element was observed in the synthesis). Sulfur element reacts with water to S₂O₃²⁻ which may be further oxidized to SO₄²⁻. Reaction 7 and 8 are proposed. It is worth mentioning that H⁺ and HS⁻ are released in both redox Reactions. Generation of HS⁻ directly enhances the precipitation of MoS₃ that is further reduced to MoS₂. Produced H⁺ lowers the pH value of final filtrate than its initial solution. Apparently, complete oxidization of sulfur to SO₄²⁻ favors high yield of MoS₂. S₂O₃²⁻ is more stable in basic aqueous solution than acid solution. S₂O₃²⁻ tends to be

Table 4. It is noticed that all the three catalysts exhibit lower CN than the MoS₂ in bulk. Similar to the spectra, the smallest CN of Mo-Mo is observed with CAT-2.5, indicating more disordered matrix on the surface.

Characterization of textural structure. The morphologies of the three catalysts with different S/Mo molar ratios are revealed by TEM (Error! Reference source not found.10). The dark thread-like lines shown in the fringes are the reflection of (0 0 2) lattice plane of the crystalline MoS₂, representing the stacked slabs. All the catalysts show dendritic morphologies and layered nanocrystallines. A large number of curved slabs are observed on the catalysts (circled in Figure 10), which may result in more defects created on the basal plane²⁰. The three catalysts have similar size distributions. Table 3 shows narrow size ranges of 15.8-17.9 nm and 2.3-2.6 nm, for the average slab length and thickness, respectively. The average lengths obtained in the present work are similar to the catalysts using (NH₄)₂MoS₄ (ATM) as precursors^{20, 10} while are significantly shorter than the crystallized MoS₂ synthesized by Li et al. who reported 50 nm in length⁸. Figure 11 shows FE-SEM images of MoS₂. For both catalysts, thread-like MoS₂ crystals are associated in bundles and twisted together forming a flower-like morphology. The images exhibit nanosized particles with an average size of 100-200 nm. Mesopores over 10 nm are formed in between the crystals, as shown in the grey part surrounded by white MoS₂ layers. A slight difference observed is that CAT-2.5 looks more dendritic, while CAT-3.75 crystal favors growth on the boundary of particles.

The three catalysts have large surface area ranging from 200 to 262 m²/g (Table 3). A high pore volume of 0.9 to 2.3 m³/g is also observed, which is much higher than that of other catalysts previously reported²⁰.

Catalytic activities. Catalysts synthesized under hydrothermal method with Na₂S and MoO₃ precursors are subjected to undergo a performance test on HDS, HDN, and hydrocracking activities, using LCO (Figures 12, 13 and 14). The initial HDS rate constants in the first hour for all catalysts are higher than 2×10^{-4} s⁻¹ g cata⁻¹. The rates drop by half in the second hour and a further 50% off was observed in the rest of the reaction. The decrease of reaction rates for each catalyst along with reaction time is due to the fact that LCO contains both easy (benzothiophene and its derivatives) and hard sulfur (dibenzothiophene and its derivatives) compounds (Table 5). Nevertheless, it is still observable that CAT-2.5 presents the highest HDS activity and CAT-3.0 has the lowest activity. CAT-3.75 positions in between. CAT-2.5 also exhibits the highest HDN (Figure 12) and hydrocracking (seen from the product density in Figure 14) ability.

The relationship between the properties and activities is plotted in Figure 15. The ratio of Mo atoms on edge to the total Mo atoms is calculated based on the slabs length, the method reported by Vrinat et al.²². Apparently, if only Mo on the edges were active sites, the activity order would be totally opposite. It is indicated that the imperfect basal plane is important for the activities, and defects should be also largely located on the curved or twisted basal plane. This can be verified with TEM images; all the catalysts show highly curved morphologies. In particular, CAT-2.5 exhibits

more blurred slabs, indicating more imperfect crystalline structure than the other two, which explains the highest activity of the three. There are also no clear relationship between activity and surface area (Figure 15 b). This statement has been mentioned by several researchers²¹. Certain surface area is essential to provide more accessible active sites, however, effect gets infinitesimal when sufficient exposed area are provided. Most of the calculated area is inert to the reaction.

As discussed in TPR, the hydrogen adsorbed is highly related to the active sites on the catalyst. From Figure 15 c, it's easy to see that there is a good linear relationship between the H₂ adsorption sites (Table 6) and HDS rate constant. The amount of active sites (as in H₂ reacted sites) reflects the catalyst activities. Similar phenomenon also can be seen from S/Mo atomic ratio macroscopically. The lack or excess of sulfur might be related to the deformation of the crystal structure and defects on the catalysts. When S/Mo ratio is lower than the stoichiometric atom ratio of MoS₂ (2), defect sites might be already generated due to the deficiency of S. On the other hand, over-stoichiometric sulfur may exist in the form of S₂²⁻ species, which can react with H₂ to form -HS species and enhance hydrotreating reaction. As more defects are created during the synthesis, the MoS₂ would deviate further from the perfect crystal, in other words, S/Mo ratio would further deviate from the stoichiometric number 2. This is consistent with our results that MoS₂ has the highest difference with largest hydrogen adsorption sites. It is also showing excellent relationship between the difference and the activities, as in Figure 15 d.

Relationship also can be seen from binding energy, coordination, disorder and activities. Although the difference is not obvious, it's also found the binding energy and MoS₂ cluster size (reflected by Mo-Mo coordination number) show the similar trend of HDS activity.

Conclusions

Novel nanocrystalline MoS₂ were successfully synthesized via hydrothermal method using commercially available MoO₃ and Na₂S. The synthesis mechanism of hydrothermal approach was investigated and the reaction pathways were proposed for the formation of crystalline MoS₂. [HS⁻] in the synthesis solution is identified as a key factor. Insufficient [HS⁻] can lead to a failure synthesis. Mild acidic medium is essential for a successful synthesis. The ratio of reactants, MoO₃ and Na₂S, is important to the nanocrystal structure and the yield. Excessive MoO₃/Na₂S ratio may result in poor uniformity of MoS₂. Various characterization techniques are employed to assess the structure of synthesized catalysts. The three catalysts synthesized at the proper range of Na₂S/MoO₃ (from 2.5 to 3.75 in the work) have nanosized structure, large surface area, and high pore volume (mesopores). More defects at the rims are found on the CAT-2.5 than the other two catalysts. HDS activity of hydrotreating LCO also exhibits a decreasing order of CAT-2.5 > CAT-3.75 > CAT-3.0.

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